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DETECTION OF AROMATIC ALDEHYDES

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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Urban atmosphere is a rich source of various types of aromatic compounds, such as phenols (1,2) and polynuclear hydrocarbons (3,4). Some evidence has also been found for the presence of quinones (2).

Our laboratory has been investigating new methods for the detection and determination of trace quantities of air-borne polynuclear hydrocarbons, phenols, quinones, carboxylic acids, and aldehydes. In the course of this investigation a method has been developed for the detection and estimation of polynuclear aromatic aldehydes. Essentially the procedure involves the reaction of the aldehyde with trifluoroacetic anhydride to form an arylidene di(trifluoroacetate). Then trifluoroacetic acid initiates condensation of the di(trifluoroacetate) with the hydrocarbon to form a diarylmethane type of dye. A fairly strong acid media is essential for complete ionization and solution of the dye.

PROCEDURE

One ml. of a solution of 5% fluoranthene in chloroform is mixed with 1 ml. of a chloroform solution thought to contain the aromatic aldehyde. Eight tenths of a milliliter of trifluoroacetic anhydride is added while the mixture is swirled. After standing for 5 minutes the mixture is diluted to 10 ml. with trifluoroacetic acid. The color can then be read and the visible absorption spectra recorded. In our work a

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Cary Model 11 Recording Spectrophotometer was used (Table I).

REMARKS

Aliphatic aldehydes, such as propionaldehyde, and ketones, such as acetophenone, do not give the color test. Similarly the o-, m- and p-nitrobenzaldehydes give negative results. The colors are stable even after 24 hours standing (Table I). The long wavelength band shifts toward longer wavelength as the aromatic aldehyde involves more fused benzene rings, e.g., benzaldehyde, 590, purple-blue; 1-naphthaldehyde, 660, blue; and 9-anthraldehyde, 790 mμ, green.

This color test opens several new lines of investigation. Thus by substituting a simple phenol or anisole for fluoranthene, dyes absorbing at shorter wavelength can be formed; with compounds such as fluorene, biphenyl, dibenzothiophene or phenyl sulfide, dyes absorbing at approximately the same wavelength can be formed; and with chrysene or anthracene, dyes absorbing at longer wavelength can be formed. With anthanthrene, benzo(a)pyrene or benzo[g,h,i]perylene dyes absorbing at a much longer wavelength can be formed. For example, in testing for piperonal with a saturated solution of anthanthrene in chloroform by the test procedure outlined, a red-brown solution was obtained with a long wavelength band at 785 mμ and a sensitivity of 0.03 micromoles/3 ml.

Alternatively using the aldehyde as a reagent the following types of aromatic compounds should also be capable of detection (or estimation) with this color reaction --- polynuclear aromatic hydrocarbons, phenols, aromatic ether, aromatic sulfides, aromatic acylamines, and heterocyclic ring systems containing ring systems such as dibenzothiophene, indole, carbazole, etc.

TABLE I

Color Reaction of Aromatic Aldehydes with Fluoranthene

Aldehyde	λmax, mμ	Color (a)	Sens. (b)
o-Phthalaldehyde	477	O	0.02
Benzaldehyde	590 (c)	P-B	2
Cinnamaldehyde	605	B	0.01
Mesitaldehyde	607	B	0.1
Anisaldehyde	610	B	0.01
o-Ethoxybenzaldehyde	612	B	0.02
Vanillin	612	B	0.05
2-Naphthaldehyde	615	B	0.2
Piperonal	627	B	0.009
1-Naphthaldehyde	660	B	0.07
1-Pyrenaldehyde	752	G	0.007
9-Anthraldehyde	790	G	0.01

(a) O = orange, P = purple, B = blue, and G = green.

(b) In micromoles/3 ml. as determined in a 1 cm. cell on a Cary Recording Spectrophotometer Model 11.

(c) Cloudy.

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